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**(54) Process for the separation of sulphur oxides from offgases.**

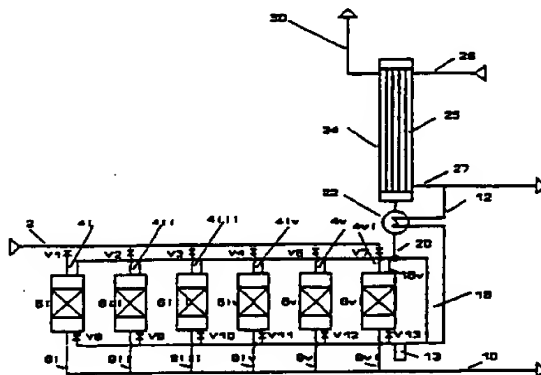
57) Process for the separation of sulphur oxides from offgases, comprising the steps of passing at a temperature from 250° C to 400° C the sulphur oxides containing offgas through a fixed bed of a sulphur oxide adsorbent, having catalytic activity in the oxidation of sulphur oxides to sulphur trioxide and comprising supported on a porous carrier a mixture of vanadium pentoxide and pyrosulphates of one or more alkali metals:

adsorbing and converting on the adsorbent sulphur oxides to sulphur trioxide;

regenerating the sulphur trioxide loaded adsorbent with air at a temperature from 500 °C to 650 °C;

recirculating a part of the regeneration air to the fixed bed of the adsorbent; and finally

removing desorbed sulphur trioxide in the regeneration air by hydration of the desorbed sulphur trioxide to sulphuric acid and condensing the sulphuric acid in a sulphuric acid condenser.



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**Field of the Invention**

This invention is directed towards a process for the separation of sulphur oxides from offgases. More particularly, the invention involves catalytic adsorption and oxidation of sulphur dioxide on a solid acceptor having catalytic activity in the oxidation of sulphur dioxide to sulphur trioxide, and removal of desorbed sulphur trioxide by conversion to sulphuric acid.

**Prior Art**

In the processes most commonly used for the removal of sulphur oxides from industrial offgases, sulphur oxides are separated from the offgases by washing with aqueous solutions or slurries of alkaline compounds, such as calcium hydroxide or calcium carbonate and sulphate, and separating the formed solid sulphites or sulphates from the offgases. Other conventionally used methods of purifying sulphur containing offgases, comprise oxidation of sulphur compounds in the offgases to sulphur trioxide and condensing the produced sulphur trioxide as sulphuric acid.

It is further known to adsorb sulphur dioxide on solid acceptors. A solid acceptor for use in the separation of sulphur dioxide from gaseous mixtures of sulphur dioxide and air is described in GB Patent No. 1,592,378. The described acceptor comprises copper and copper oxides promoted with platinum and rhenium on alumina-carrier material. When contacted with sulphur dioxide containing air, the acceptor is stated to retain up to 98% of sulphur dioxide, with a regeneration efficiency of the loaded acceptor of up to 98% at elevated temperature in the presence of a reducing gas.

Sulphur dioxide separation by alternate adsorption-desorption cycles is disclosed in Us Patent No. 3,989,798, where in a first cycle sulphur dioxide in offgas is adsorbed on a vanadium oxide adsorbent, and in a subsequent cycle desorbed by contact with a reducing gas.

As a general drawback of the known adsorption processes, adsorbed sulphur oxides are liberated by reducing gases. Use of reducing gases, such as hydrogen and carbon monoxide, for regeneration of spent adsorbents is detrimental for the overall process economy. Preparation of these gases is an energy consuming process, which causes high process costs.

We have now found that the overall process economy of adsorption processes for the removal of sulphur oxides in offgases is much improved, when using a solid sulphur oxide adsorbent, which is regenerable by air, and from which adsorbed sulphur oxides are desorbed as sulphur trioxide during regeneration.

**Summary of the Invention**

A broad embodiment of this invention is directed towards an improved adsorption process for the separation sulphur oxides from offgas, comprising the steps of,

passing at a temperature from 250 °C to 400 °C the sulphur oxides containing offgas through a fixed bed of a sulphur oxide adsorbent, having catalytic activity in the oxidation of sulphur oxides to sulphur trioxide and comprising supported on a porous carrier a mixture of vanadium pentoxide and sulphates of one or more alkalimetals;

adsorbing and converting on the adsorbent sulphur oxides to sulphur trioxide;

regenerating the sulphur trioxide loaded adsorbent with air at a temperature from 500 °C to 650 °C;

recirculating a part of the regeneration air to the fixed bed of the adsorbent; and finally

removing desorbed sulphur trioxide from the regeneration air by hydration of the desorbed sulphur trioxide to sulphuric acid and condensing the sulphuric acid in sulphuric acid condenser.

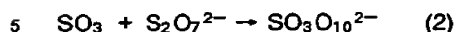
In a preferred embodiment of the invention the sulphur oxide adsorbent comprises a porous silica carrier with vanadium pentoxide and pyrosulphates of alkalimetals loaded in its pore system.

A particular preferred adsorbent for use in the inventive process comprises a porous silica carrier with a pore volume of between 0.3-1 cm<sup>3</sup>/g loaded with 5-9 wt% vanadium pentoxide and the pyrosulphates of sodium and potassium in a molar ratio of K/V of 2-4 and Na/V of 0-1, as commercial available from Haldor Topsøe A/S, Denmark, sold under the tradename "VK-Catalyst", either in the form of ring shaped catalyst particles or as monolithic blocks with straight channels through the blocks.

In the operation of the process, sulphur oxides in the offgas, typically in the form of SO<sub>2</sub>, are in a first process step catalytically oxidized to SO<sub>3</sub> at a temperature of between 250-400 °C by contact with vanadium pentoxide according to the reaction:

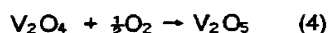
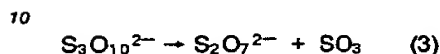


Formed  $\text{SO}_3$  is then adsorbed by the pyrosulphate in the pore system of the adsorbent through conversion of pyrosulphate to higher pyrosulphates:



Spent adsorbent, loaded with sulphur trioxide is in a subsequent process step, regenerated with air.

At temperatures above  $500^\circ\text{C}$   $\text{SO}_3$  desorbs from the pyrosulphates and vanadium tetroxide is oxidized to vanadium pentoxide, according to the following reaction scheme:



As mentioned hereinbefore the basic concept of the invention relates to the reduction of process costs in the removal of sulphur oxide. This is obtained in the above process through concentrating the content of sulphur oxides in the offgas to be cleaned by adsorption on a solid adsorbent-catalyst as described above and desorption of produced sulphur trioxide from the adsorbent into a much reduced volume of air compared to the volume of offgas and by recirculating a part or most of the regeneration air back to the adsorbent.

Desorbed sulphur trioxide in the regeneration air is finally removed from the air by hydration of sulphur trioxide to sulphuric acid vapours and condensation of the formed sulphuric acid vapours in a sulphuric acid condenser.

A particular suitable sulphuric acid condenser for use in the inventive process is the heat exchanger-sulphuric acid condenser described in PCT Patent Application No. PCT/DK89/00129, the entire enclosure of which is incorporated herein by reference.

Depending on the amount of air used during the regeneration of the adsorbent and on the recycle factor, the size of the sulphuric acid condenser for the final removal of sulphur trioxide is diminished in the order of 10-25 times, when compared to condensers employed in offgas desulphurization processes by which  $\text{SO}_2$  is continuously oxidized to  $\text{SO}_3$  followed by hydration of  $\text{SO}_3$  and condensation of formed sulphuric acid vapours from the offgas.

The inventive process may advantageously be performed in continuous manner in at least two beds of the adsorbent operating in parallel, such as at least one bed is stepwise operated in adsorption mode, and at least a second bed stepwise in regeneration mode.

### Detailed Description

The above as well as other features and aspects of the invention will become more evident from the following, detailed description and the attached drawing, in which the sole Figure represents a simplified flow diagram of a specific embodiment of the inventive process.

The Figure shows a flow diagram of a desulphurization plant employing 6 adsorption reactors operating in parallel, with one reactor always under regeneration. During regeneration the reactors are connected to a sulphuric acid condenser as described in more detail in the aforementioned PCT Patent Application No. PCT/DK89/00129.

In a first operation cycle sulphur oxides containing offgas in line 2 is distributed at a temperature of between  $250^\circ\text{C}$  and  $450^\circ\text{C}$  to reactors 61-66 through valve guided lines 41-46.

Reactor 66 is in this cycle under regeneration as further described below. Each of reactors 61-66 is loaded with a fixed bed of the above commercial Haldor Topsøe  $\text{SO}_2$ -adsorbent-catalyst in the form of monolithic blocks with straight channels of 6 mm hydraulic diameter. During its passage through reactors 61-66,  $\text{SO}_2$  in the gas is oxidized and adsorbed on the adsorbent-catalyst, and substantially sulphur-free gas leaves the reactors in lines 81-86 and is vented to the atmosphere through line 10.

Reactor 66 containing in this cycle spent adsorbent-catalyst from a previous adsorption cycle is regenerated by air at a temperature of from  $350$ – $600^\circ\text{C}$  supplied on line 12 and recirculation line 18.

During regeneration with hot air,  $\text{SO}_3$  adsorbed on the adsorbent-catalyst is desorbed as described in detail herein before.  $\text{SO}_3$  loaded regeneration air is then withdrawn from reactor 66 through valve V13. A part of this air is recirculated through line 18, and mixed with further air from line 12.

The remaining part of the spent regeneration air is sent in line 20 to sulphuric acid condenser 24.

At high regeneration temperatures a part of the  $\text{SO}_3$  may decompose to  $\text{SO}_2$ . Therefore, the

regeneration air being passed to the sulphuric acid condenser is optionally send to a catalytic oxidation step (not shown in the Figure), wherein  $\text{SO}_2$  is oxidized to  $\text{SO}_3$  by contact with a conventional sulphuric acid catalyst before the gas is introduced into condenser 24.

Sulphuric acid condenser 24 is provided with a plurality of glass tubes 25 being externally cooled with air.

In condenser 24, the spent regeneration air flows inside tubes 25 in indirect heat exchange with the cooling air introduced into condenser 24 through line 26. Thereby,  $\text{SO}_3$  in the air is condensed in the tubes to sulphuric acid as further described in PCT Patent Application No. PCT/DK89/00129.

Desorbed  $\text{SO}_3$  and water contained in the spent regeneration air being passed to condenser 24, are condensed as sulphuric acid in air cooled tubes 25. After having passed through tubes 25 cleaned regeneration air leaves condenser 24 and is vented to the atmosphere through line 30.

The cooling air flows on the outside of tubes 25 countercurrently to the spent regeneration air in the tubes. After having cooled the tubes, the cooling air is withdrawn from tower 24 through line 27. A part of the withdrawn cooling air is looped to line 12 and used in this process cycle as fresh regeneration air for reactor 66. Before being introduced into reactor 66 the air is preheated in heat exchanger 22 by indirect heat exchange with the spent regeneration air from reactor 66. The preheated air is mixed with recirculated regeneration air from line 18 and the combined stream air further heated by burner 13 before being introduced into the reactor.

Subsequent purification cycles are carried out in similar manner to that described above. In each cycle always 5 reactors are under adsorption and one under regeneration. The valve sequence for 6 consecutive process cycles is shown in Table 1.

Table 1

Reactors								Valves											
	61	62	63	64	65	66		V1	V2	V3	V4	V6	V7	V8	V9	V10	V11	V12	V13
	Ad	Ad	Ad	Ad	Ad	R		O	O	O	O	O	C	C	C	C	C	C	O
	Ad	Ad	Ad	Ad	R	Ad		O	O	O	O	C	O	C	C	C	C	O	C
	Ad	Ad	Ad	R	Ad	Ad		O	O	O	C	O	O	C	C	C	O	C	C
	Ad	Ad	R	Ad	Ad	Ad		O	O	C	O	O	O	C	C	O	C	C	C
	Ad	R	Ad	Ad	Ad	Ad		O	C	O	O	O	O	C	O	C	C	C	C
	R	Ad	Ad	Ad	Ad	Ad		C	O	O	O	O	O	O	C	C	C	C	C

Ad = Adsorption

O = Open

R = Regeneration

C = Closed

## 55 Example

Offgas containing 600 ppm SO<sub>2</sub>, about 7% H<sub>2</sub>O and about 4% O<sub>2</sub> is treated in the above described reactor system. A total of 10<sup>6</sup> Nm<sup>3</sup>/h of the offgas is distributed at a temperature of 350 °C to reactors 61-

65, which are operated in adsorption mode. Reactor 66 is under regeneration. Each of reactors 61-66 is loaded with  $41 \cdot 10^3$  kg of the aforementioned VK adsorbent-catalyst having an adsorption capacity of about 0,05 kg SO<sub>3</sub>/kg adsorbent-catalyst. By passage through reactors 61-65 570 Nm<sup>3</sup>/h SO<sub>2</sub> in the offgas are adsorbed on the adsorbent-catalyst during an adsorption period of 5 hours. The content of SO<sub>2</sub> in the offgas is, thereby, reduced by 95% resulting in a cleaned gas with 30 ppm SO<sub>2</sub> and about 5 ppm SO<sub>3</sub>.

Regeneration of the reactors (in this Example reactor 66) is carried out with air flowing in opposite direction to that of the offgas during the adsorption period. 39,000 Nm<sup>3</sup>/h of the cooling air leaving tower 24 are used for the regeneration.

The cooling air leaving condenser 24 at a temperature of about 205 °C is preheated to about 377 °C in heat exchanger 22. During the first 30 minutes of the regeneration period the air is mixed with 40,000 Nm<sup>3</sup>/h of spent regeneration air being recycled from the exit of reactor 66. The total flow of 79,000 Nm<sup>3</sup>/h air is further heated to 580 °C in burner 13 upstream to reactor 66. By passage of the hot air the reactor is heated and hot waves move through the adsorbent bed. After 30 minutes, about 40,000 Nm<sup>3</sup> of hot air have passed through the reactor and hot waves are breaking through the reactor. Recirculation and the burner are then stopped and the reactor is flushed at about 377 °C with 39,000 Nm<sup>3</sup>/h of the preheated cooling air from tower 24 for the next 30 minutes of the regeneration period.

After a total of 60 minutes the regeneration valve V13 is closed.

During regeneration of reactor 66 adsorbed SO<sub>3</sub> is desorbed into a stream of 40,000 Nm<sup>3</sup>/h of regeneration air.

The regeneration air being passed to the sulphuric acid condenser is sent to a catalytic SO<sub>2</sub> oxidation step prior to introduction into condenser 24. After oxidation of SO<sub>2</sub> to SO<sub>3</sub>, the regeneration air contains 1,41% SO<sub>3</sub>, 0,014% SO<sub>2</sub> and about 3% H<sub>2</sub>O and is desulphurized in condenser 24. Before being introduced into condenser 24, the temperature of the spent regeneration air is adjusted to 270 °C by indirect heat exchange as mentioned above.

In condenser 24 most of the SO<sub>3</sub> contained in the spent regeneration air is condensed as sulphuric acid, which is withdrawn through line 32 at the bottom of the condenser. The cleaned regeneration air containing now about 5 ppm SO<sub>3</sub> and 145 ppm SO<sub>2</sub> leaves tower 24 through line 30.

## Claims

1. Process for the separation of sulphur oxides from offgases, comprising the steps of
  - passing at a temperature from 250 °C to 400 °C the sulphur oxides containing offgas through a fixed bed of a sulphur oxide adsorbent, having catalytic activity in the oxidation of sulphur oxides to sulphur trioxide and comprising supported on a porous carrier a mixture of vanadium pentoxide and pyrosulphates of one or more alkalimetals;
  - adsorbing and converting on the adsorbent sulphur oxides to sulphur trioxide;
  - regenerating the sulphur trioxide loaded adsorbent with air at a temperature from 500 °C to 650 °C;
  - recirculating a part of the regeneration air to the fixed bed of the adsorbent; and finally
  - removing desorbed sulphur trioxide in the regeneration air by hydration of the desorbed sulphur trioxide to sulphuric acid and condensing the sulphuric acid in a sulphuric acid condenser.
2. The process of claim 1, wherein the sulphur oxide adsorbent comprises a porous silica carrier with vanadium pentoxide and pyrosulphates of alkalimetals loaded in the pore system of the carrier.
3. The process of claim 2, wherein the sulphur oxide adsorbent comprises a porous silica carrier with a pore volume of between 0,3-1 cm<sup>3</sup>/g loaded with 5-9 wt% vanadium pentoxide and the pyrosulphates of sodium and/or potassium in a molar ratio of K/V of 2-4 and Na/V of 0-1.
4. The process of claim 1, wherein the sulphuric acid condenser for removing sulphur trioxide contained in the regeneration air is provided with a plurality of tubes being externally cooled by air flowing countercurrently and in indirect heat exchange with the regeneration air inside the tubes.
5. The process of claim 4, wherein a part of the cooling air leaving the sulphuric acid condenser is used as regeneration air during regeneration of the adsorbent.
6. The process of claim 1, wherein the adsorbent is in the form of monolithic blocks with parallel channels having a hydraulic diameter of 3-10 mm, preferably 5-7 mm, for passage of the offgas.

7. The process of claim 1, wherein the stream of regeneration air leaving the regeneration step is passed before the sulphuric acid condenser through a reactor loaded with a sulphuric acid catalyst.
8. The process of claim 7, wherein the sulphuric acid catalyst is in the form of monolithic blocks with parallel channels for passage of the gas, the equivalent diameter of the channels being 3-10 mm, preferably 5-7 mm.

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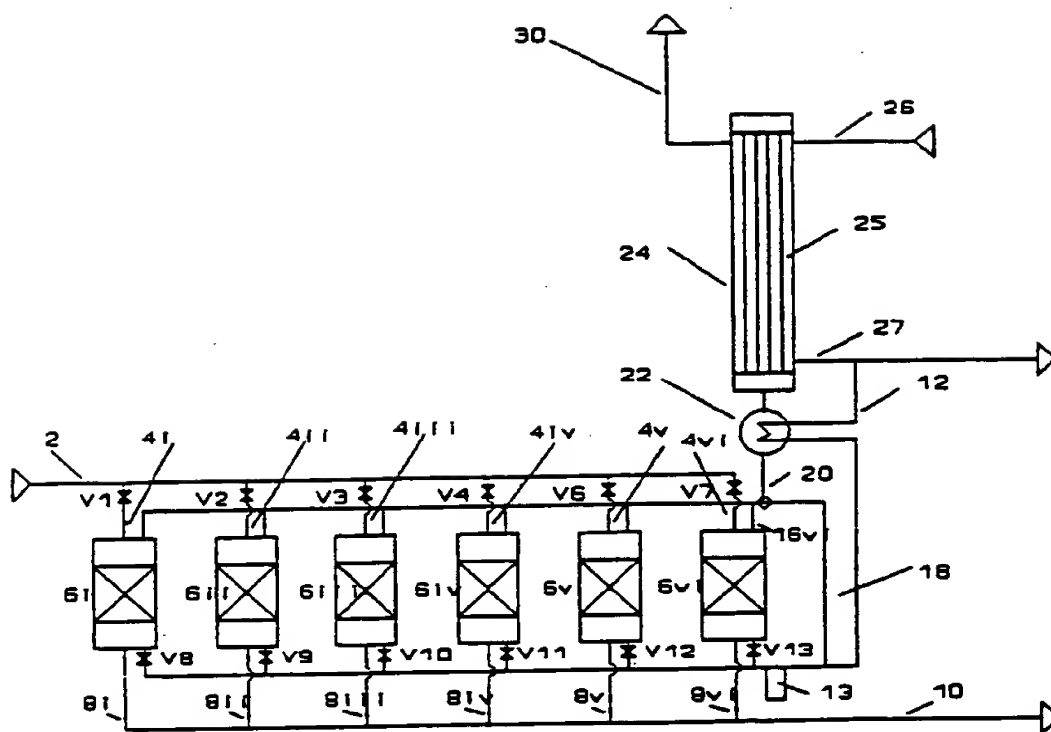
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## EUROPEAN SEARCH REPORT

Application Number

EP 92 10 8710

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Y	US-A-3 615 196 (WELTY ET AL.) * column 3, line 4 - line 21 * * column 5, line 1 - line 29; claims 1-8; figures 1,2 *	1-5,7	B01D53/36 C01B17/79 C01B17/76
Y	WO-A-8 912 025 (HALDOR TOPSOE A/S) * page 6, line 25 - page 7, line 5; claim 10; figures 1,3 *	1-5,7	
A	US-A-4 781 902 (HALDOR TOPSOE A/S) * column 2, line 55 - column 4, line 9 * * column 4, line 36 - line 39 *	1-3,6	
A	GB-A-2 051 761 (HALDOR TOPSOE A/S) * page 1, line 40 - line 44 * * page 2, line 15 - line 38 * * page 2, line 53 - page 3, line 6; figure 2 *	1,2,7	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			B01D B01J C01B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 AUGUST 1992	Examiner EIJ KENBOOM T.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

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